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Biodiesel production from heterotrophic microalgae through transesterification and nanotechnology application in the production

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ABSTRACT

Vegetable oils and animal fats are the most often used feedstock in biodiesel production; however, they are also used in food production, which results in increasing the feedstock price due to the competition. Therefore, alternative feedstock is required in biodiesel production. Heterotrophic microalgae are found capable of accumulating high lipid (up to 57% w/w). They can use complex carbons such as sweet sorghum and Jerusalem artichoke as nutrients to produce equivalent quantity oil as that of using glucose, which provides a cheap biodiesel production strategy. It was found that nanomaterials could stimulate microorganism metabolism, which suggested that nanomaterial addition in the cultivation could enhance lipid production of microalgae. Furthermore, the use of nanomaterials could improve the efficiency of the lipid extraction and even accomplish it without harming the microalgae. Nanomaterials such as CaO and MgO nanoparticles have been used as biocatalyst carriers or as heterogeneous catalyst in oil transesterification to biodiesel. In this paper, the factors that could impact on lipid accumulation of heterotrophic microalgae are critically reviewed; the advances on application of nanotechnology in microalgae lipid accumulation, extraction, and transesterification are addressed.

Contents

1. Introduction

At present, transesterification using plant oils, animal fats, or lipids from oleaginous microalgae is the major method of biodiesel production [1–3]. Among all the feedstock, oleaginous microalgae have gained a growing interest because of that conventional feedstock, plant oils which at present are the main source of biodiesel production, is becoming more and more unsustainable due to the strong competition with food production and kitchen utilization. The faster growth rate and greater lipid content of microalgae compared to oilseed crops urge researchers to develop the microalgae utilization in biodiesel production instead of plant oils [2,4]. In addition, the possibility of increasing lipid content of microalgae by controlling their cultivation condition, while which

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is not possible for plant, offers another significant advantage [5]. Rodolfi et al. [6] selected four among 30 strains of microalgae to investigate the impact of cultivation condition such as irradiation and nutrient on lipid accumulation of the microalgae and found that lipid content significantly varied with the change of cultivation conditions.

Numerous studies have been reported on autotrophic microalgae used for production of biodiesel [7,8]. Autotrophic microalgae are capable of using carbon dioxide and solar energy to synthesize organics such as protein and lipid for their growth. Most of the production of autotrophic microalgae for biodiesel production occurs in indoor photobioreactors. The heavily light-dependent growth characterization of autotrophic microalgae resulting in energy consuming for illumination, as well as the low efficiency in the biomass productivity, has hindered autotrophic microalgae application in biodiesel production. In comparison, heterotrophic microalgae are more flexible for the cultivation condition (can grow under light free condition), and was found capable of accumulating higher lipid in the cells [9–11]. Miao and Wu [9] reported that the lipid content of heterotrophic *Chlorella protothecoides* was 3 times higher than that of the autotrophic one. Up to now, *Chlorella protothecoides* is the most studied heterotrophic algae as lipid source for biodiesel production [12–14].

Nanotechnology is the technique to devise, synthesize, manufacture and apply the matters with atomic or molecular precision at dimensions of 100 nm (nm) or smaller [15]. Nanomaterials have the surface area several hundred times more than their equal weight of macroscale materials. Not only is the surface area extensively increased, the tenacity, elasticity, strength and electricity are also enhanced.

There are many research fields and several potential applications that involve nanotechnology due to its unique behaviors and properties. Nanotechnology application in biodiesel production from microalgae mainly includes nanomaterial utilization on lipid accumulation, extraction and on the transesterification process as catalyst support or catalyst as shown in Fig. 1 [16–19]. In tradition, organic solvents having great affinity to lipid such as chloroform, hexane, isopropanol, and methanol are utilized in lipid extraction from microalgae; however, the use of toxic material (solvents), the difficulty of the complete recovery of the material, and the demand of the energy intense solvent–lipid separation step requires the development on extraction technology. The mechanism of solvent extraction is that solvent can weaken/break cell wall, and thus enhance lipid diffusion to the outer environmental/dissolve the lipid. Nanomaterials are favorable carriers in immobilization due to the high surface area, and solid nanomaterials can be easily recovered from liquid phase by filtration or centrifugation. Therefore, immobilizing organic solvent-like chemicals onto solid nanomaterials would solve the problems in organic solvent extraction. The immobilized chemicals as function group achieve the lipid extraction and were recovered as nanomaterials were recovered. A research revealed that modified nanosphere silica accomplished the extraction from alive microalgae which would be sent back for lipid accumulation again, and hence the process avoids recultivation [16]. It would be the immobilization of chemicals which weaken the cell wall (but not to kill the microalgae) and would thus lead to lipid diffusion from inside to outside of the cells.

The most employed catalyst in transesterification is acid or base; however, the corrosion (aggressive acid utilization) and soap formation (free fatty acid reacts with base) need alternative catalysts. Lipase, a biocatalyst, is environmentally friendly and efficient, but rather expensive, while the cost can be reduced when lipase immobilization is applied because of the possibility of lipase reuse. Nanomaterials have large surface area for immobilization and can be easily separated from products, hence, immobilizing

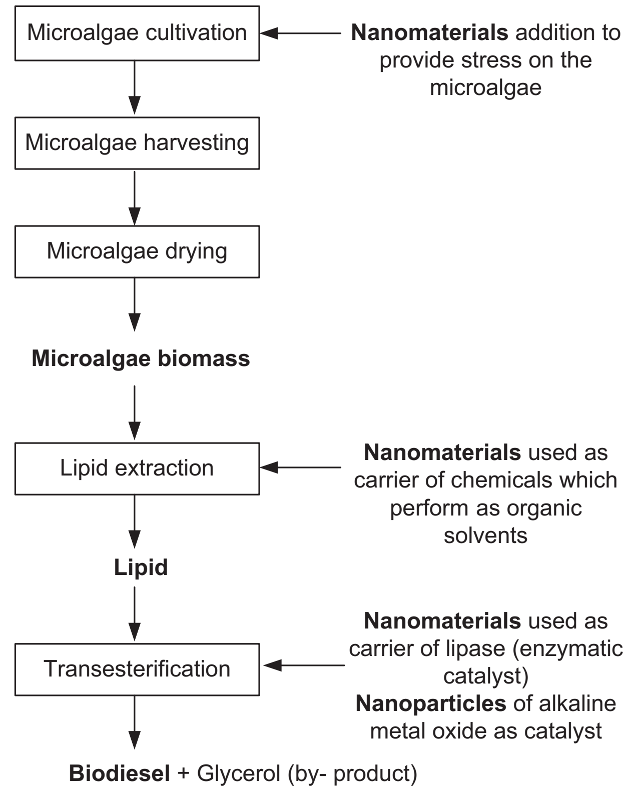

Fig. 1. Nanotechnology application in biodiesel production from heterotrophic microalgae.

lipase onto nanomaterials would benefit reducing the cost of using lipase [20]. Apart from being carriers, nanomaterials such as CaO, Al_2O_3, and MgO nanoparticles themselves are heterogeneous catalysts and can achieve high conversion rate (> 99%) with less addition amount (< 1% of oil addition) [21,22]. It is contributed by its high surface area which increased contacting chances with the reagent lipid. Moreover, comparing with the bulk materials, activity, lifetime, and resistance to poisons of their nanomaterials are improved [23,24]. Therefore, it suggested that nanomaterials catalysts could have high performance in transesterification.

Biodiesel production from heterotrophic microalgae includes microalgae lipid production (also called feedstock production) and the lipid transesterification to biodiesel. The lipid production including lipid accumulation and extraction is essential step as feedstock takes up to 70% of the overall cost [25,26]. Researchers have reviewed the methods including cultivation temperature, pH, the presence of radiation, and nutrient limitation, for enhancing lipid accumulation in microalgae [27]. Carbon and nitrogen source, carbon to nitrogen ratio, mineral presence, and the nanomaterial effect on the lipid accumulation have not been well addressed. The review on organic solvent extraction or pre-treatment (sonication, homogenization, microwave, bead milling) followed by solvent extraction for lipid extraction from microalgae have been reported [28,29]. Nanomaterial application on the extraction has not been discussed. Transesterification of lipid to biodiesel with various catalysts, the homogeneous and the heterogeneous, has been well analyzed [30,31]. Nanomaterial as a promising catalyst in transesterification should be paid significant attention. In this paper, the factors that could impact on lipid accumulation of heterotrophic microalgae are critically reviewed, and the advances of nanomaterial's application in lipid production are addressed. Additionally, the potential application of nanomaterials in biodiesel synthesis (transesterification) is proposed as well.